

Band gap of Ge rich $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys

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$\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ films ($x \approx 0.90$, $y \leq 0.02$) were grown by molecular beam epitaxy on Si substrates. Infrared optical absorption was used to obtain the band gap energy at room temperature. Biaxial strain obtained from x-ray diffraction measurements verified the presence of nearly relaxed films, and the total and substitutional C contents were obtained from channeling C-resonance backscattering spectrometry. We show by direct measurements that interstitial C had a negligible impact on the band gap, but substitutional C was found to increase the band gap with respect to equivalently strained $\text{Si}_{1-x}\text{Ge}_x$ alloys. While strain decreases the band gap, the effect of substitutional C on the band gap depends on the Si and Ge fractions. © 1996 American Institute of Physics. [S0003-6951(96)04343-4]

The energy band gaps of group IV alloys have been studied by photoluminescence (PL),^{1,2} absorption,³⁻⁵ spectroscopic ellipsometry,^{6,7} and theoretical techniques.⁸⁻¹⁰ Several studies suggest an energy band gap decrease as the C content is increased,^{6,9} others suggest an increase in the energy band gap.^{4,8} Attempts to clarify this behavior have depended on measurements of strained pseudomorphic thin layers with extrapolations to zero strain based on assumption of deformation potentials, which are not well known.

In this letter, we studied relaxed layers with Ge rich compositions. Techniques to probe the indirect optical band gap by absorption are challenged by weaker absorption than a direct band gap material, substrate absorption, and interference fringes within the thin film. We describe an approach to deducing the band gap from optical absorption observations which to some extent transcend these difficulties.

We have produced a series of crystalline $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys by solid source molecular beam epitaxy (MBE) on (100) Si substrates.^{4,11} The substrate temperature was 600 °C. Ge was thermally evaporated in a pyrolytic boron nitride crucible at 1260 °C, and Si was thermally evaporated in a pyrolytic graphite (PG) crucible at 1685 °C. The C source consisted of a PG filament heated by a direct current up to 49 A. Growth rates were typically 0.06 $\mu\text{m}/\text{h}$. Thicknesses were measured by a mechanical stylus method and were typically 0.18 μm .

Film compositions (Table I) were measured by Rutherford backscattering spectrometry (RBS). C elastic-resonance backscattering was used to measure the C concentration using a 4.3 MeV He beam. The total measured C concentrations were up to 2 at. %, with an accuracy of ± 0.2 at. % C. The extent of substitutional C was studied using ion channeling characterizations. In samples SGC-67, SGC-68, and SGC-70, less than 25% of the C was substitutional, but at least 70% of the total C in SGC-69 was found to be substitutional. Further RBS details will be published elsewhere.¹²

X-ray diffraction (XRD) measurements were performed to determine the strain in the films. The lattice constants of the films in the growth direction (a_{\perp}) were computed from the peak position of the alloy (004) x-ray reflections. The lattice constants in the direction parallel to the substrate surface (a_{\parallel}) were deduced from the (224) and (115) reflections. Assuming Poisson's ratio to be 0.27, we calculated the relaxed cubic lattice constant (a_0) and the biaxial strain for each sample. We observed $a_{\perp} - a_{\parallel} < 0.03$ Å for all samples, indicating nearly relaxed films. Relaxed films were expected as the films were well over the 20 Å critical thickness¹³ of Ge rich Si alloys.

The optical absorption at photon energies near the band gap was measured at room temperature by Fourier transform infrared (FTIR) spectroscopy. The alloys studied were Ge rich, thus their band gap energies were less than that of Si, and the substrates were transparent in the vicinity of the alloy's fundamental absorption edge. The transmission data of the samples were ratioed to transmission curves of a reference substrate to remove sub-gap substrate absorption errors.

TABLE I. The effect of substitutional and interstitial C on the energy band gap of Ge rich $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys. The Si, Ge, and total C content of each sample was measured by RBS. The strain in each thin film was obtained from XRD, and the experimental band gaps were obtained by curve fitting to the fundamental absorption edge. The band gap of each sample was compared to a hypothetical $\text{Si}_{1-x}\text{Ge}_x$ alloy with the same Si:Ge ratio and strain (far right column). Over 70% of the C in sample SGC-69 was substitutional; the other samples had less than 20% substitutional C. Thus, substitutional C increased the band gap, and interstitial C had a negligible effect on the band gap.

Sample	Composition	Strain	Band gap (meV)	Equivalently strained
				$\text{Si}_{1-x}\text{Ge}_x$ band gap (meV)
SGC-67	$\text{Si}_{0.135}\text{Ge}_{0.845}\text{C}_{0.02}$	1.5×10^{-3}	889 ± 3	896
SGC-68	$\text{Si}_{0.11}\text{Ge}_{0.88}\text{C}_{0.01}$	1.5×10^{-3}	866 ± 5	867
SGC-69	$\text{Si}_{0.11}\text{Ge}_{0.88}\text{C}_{0.01}$	3.0×10^{-3}	895 ± 9	850
SGC-70	$\text{Si}_{0.10}\text{Ge}_{0.88}\text{C}_{0.01}$	1.5×10^{-3}	854 ± 7	856

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A model of thin film absorbance in the presence of interference fringes was applied to deduce an absorption coefficient free of interference fringe effects.¹⁴ The transmittance of a thin absorbing film on a substrate is given by

$$T = \frac{(t_1 t_2)^2 e^{-\alpha d}}{1 + (r_1 r_2)^2 e^{-2\alpha d} + 2r_1 r_2 e^{-\alpha d} \cos(2\phi - \pi)}, \quad (1)$$

where r_1 , t_1 , r_2 , and t_2 are the Fresnel reflection and transmission coefficients of the alloy/air and alloy/substrate interfaces, $\phi = 2nd(1/\lambda)$, d is the alloy layer thickness, and λ is the vacuum wavelength of the incident photons.

For the purposes of data analysis, α was assumed to be negligible below the energy onset of fundamental absorption. Thus the exponentials of Eq. (1) reduced to unity at sub-gap energies, the amplitude of the fringes was determined solely by the index of refraction (n), and the fringe periodicity (ϕ) was determined by n and d . These parameters were determined by curve fitting the transmittance data in the sub-gap region ($\alpha=0$) to the following expression:

$$T = \frac{(t_1 t_2)^2}{1 + (r_1 r_2)^2 + 2r_1 r_2 \cos(2\phi - \pi + \psi)}. \quad (2)$$

We have introduced a phase shift fitting parameter (ψ), because we observed a phase shift in the interference fringes and were able to more effectively remove the interference from the absorption data by including it. In perfect crystals with real indices of refraction, ψ is expected to be zero. We speculated that the alloy layers were not fully homogeneous, having grain boundaries and voids. Scattering within the alloy layer may be responsible for this phase shift in the interference fringes.

For indirect semiconductors at photon energies below and near the band gap, n is nearly real and constant.¹⁵ We fixed n (hence r_1 , t_1 , r_2 , and t_2) in Eq. (1) at the sub-gap values obtained from the fringes, and Newton's method was applied to solve Eq. (1) for α , given T . This yielded α free from interference fringes.

Because the smaller values of α were obscured by noise, curve fitting was adopted to deduce the band gap from the more strongly absorbing energies. The absorption data were initially fit to

$$\alpha = K(E_G - h\nu_{pt})^m \quad (3)$$

with material constant K , band gap E_G , and exponent m taken as adjustable fitting parameters, to determine the mode of the electron transition. Minimum residual error (χ^2) yielded $m \approx 2$ for all samples, indicating indirect band gap materials. For sample SGC-69, which had a significant substitutional C content, the residual error was minimized for $1.9 < m < 2.1$. The fit for the remaining samples converged to $n \approx 2$ less strongly, with comparable values of χ^2 obtained for $1.5 < m < 2.0$.

Therefore we fixed the exponent at $m=2$ and repeated the curve fit to the following relation:

$$\alpha_a = K(h\nu_{pt} + h\nu_{pn} - E_G)^2, \quad (4)$$

$$\alpha_e = K \left[\exp\left(\frac{h\nu_{pn}}{kT}\right) (h\nu_{pt} - h\nu_{pn} - E_G)^2 \right], \quad (5)$$

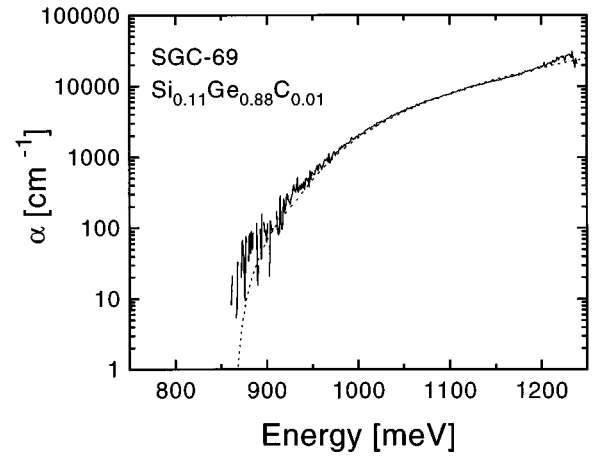


FIG. 1. Optical absorption of SGC-69. Experimental data are indicated by a solid line and the best fit of a theoretical indirect absorption curve is indicated by a dashed line. An excellent fit was obtained, and a band gap of 895 ± 9 meV was deduced from this curve fit.

$$\alpha = \begin{cases} \alpha_e + \alpha_a & h\nu_{pt} - h\nu_{pn} \geq E_G, \\ \alpha_a & h\nu_{pt} + h\nu_{pn} \geq E_G > h\nu_{pt} - h\nu_{pn}, \\ 0 & h\nu_{pt} + h\nu_{pn} < E_G, \end{cases} \quad (6)$$

where α_a and α_e are the photon absorption contributions from the phonon absorption and phonon emission processes, respectively, $h\nu_{pt}$ and $h\nu_{pn}$ are the photon and phonon energies, kT is the thermal energy and K includes several material and physical constants. Adjustable fitting parameters included E_G , K , and $h\nu_{pn}$.

Absorption data and the best fit for sample SGC-69 are illustrated by Fig. 1. The data points were unweighted, so the fitting algorithm favored data points with large values of α . Figure 2 shows a comparison between SGC-69 and SGC-68, a sample with predominantly interstitial C. A sub-gap absorption tail is evident in SGC-68, with the theoretical ab-

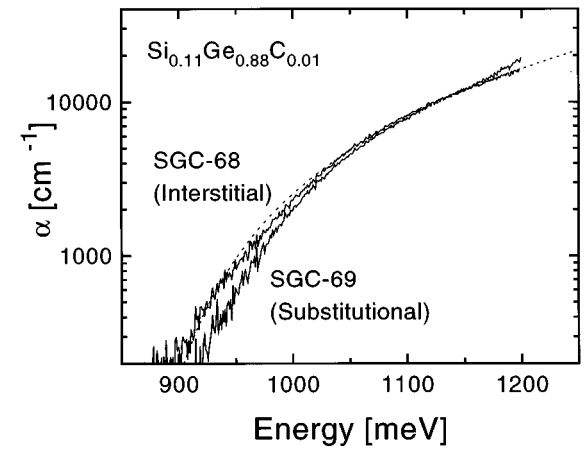


FIG. 2. Optical absorption of SGC-68. This sample has the same composition as the sample in Fig. 1, however the C is primarily interstitial. The solid line indicates experimental data and the dashed line indicates the best fit of an indirect absorption curve. The band gap of this sample is lower, and an absorption tail near $\alpha = 100 \text{ cm}^{-1}$ was evident by the departure of the experimental data from the theoretical absorption curve at low energies. The absorption curve of SGC-69 was included for comparison.

sorption curve departing from the experimental data at low energies. Results for SGC-67 and SGC-70 were similar. The absorption tail was not present in SGC-69 (Fig. 1), which has the same composition as SGC-68 but a higher substitutional C content. Fitting results indicated $h\nu_{\text{pn}} \approx 25$ meV for all samples.

During the growth of SGC-69 the C filament was off, thus we conclude that the source of C was the PG crucible used to contain the Si. We speculate that the co-evaporation of Si and C from the crucible favored substitutional C. The C filament was heated to approximately 2000 °C during the growth of the other samples. Further study is necessary to determine the mechanism by which the presence of this C molecular beam caused a decrease in substitutional C.

For Si rich, strained $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ thin films on Si substrates, C can be viewed as altering the band structure through strain reduction.¹ But the Ge rich alloys studied here are nearly relaxed. Thus bulk strain reduction is not predominantly responsible for the shift in the absorption edge we observed.

The band gap energy of each sample was compared to a hypothetical $\text{Si}_{1-x}\text{Ge}_x$ alloy with the same Si:Ge ratio and the same strain. The band gap was computed as $E_G(L) = 0.7596 + 1.0860(1-x) + 0.3306(1-x)^2$.¹⁵ The small residual strain measured by XRD for each $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ sample was applied to an established deformation potential relation for the strained $\text{Si}_{1-x}\text{Ge}_x$ system¹⁶ to obtain the hypothetical $\text{Si}_{1-x}\text{Ge}_x$ band gap with the same strain as our $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys (Table I). With this approach, it is not necessary to assume a deformation potential for $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$, which is not yet known. The samples with predominately interstitial C had band gaps similar to the equivalently strained $\text{Si}_{1-x}\text{Ge}_x$ alloy. In SGC-69, the substitutional C was found to increase the energy band gap by 45 meV/%C, which we attribute to the effect of alloying.

We have grown a series of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ thin films ($x \approx 0.90$, $y \leq 0.02$) by MBE and conducted an experimental study of their energy band gaps. The location of the C in the crystal was found to impact the energy band gap of the ma-

terial, which supports the assertion that C may be used to tune the band gap. Substitutional C was found to increase the band gap at this composition. Other workers have found C decreases the band gap with respect to a $\text{Si}_{1-x}\text{Ge}_x$ alloy. However, other work has been limited to Si rich alloys, and the band gap may in fact decrease with increasing substitutional C at those compositions. Thus, this work is not necessarily inconsistent with previous results.

The location of C within a Ge rich $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ lattice is evidently dependent on the growth conditions. The ability to manipulate the growth conditions to increase the substitutional C incorporation will allow the $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ band gap and lattice constant to be engineered over a wider composition range.

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